S2-2 Thiogallate phosphors for phosphor-converted LEDs: saturated green emission

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ABSTRACT

Phosphor-converted white light-emitting diodes (pcLEDs) are now commonly used in general lighting and display backlighting. For the latter application, red and green phosphors with saturated colours are preferred to reduce filtering losses. In this paper we report on our studies on green-emitting thiogallate phosphors ($ZnGa_2S_4$:Eu and $SrGa_2S_4$:Eu) with narrow emission bands.

1. INTRODUCTION

Solid state lighting based on LEDs (light-emitting diodes) is quickly replacing other lighting technologies, such as incandescent lamps and fluorescent lights (tubes, CCFLs,…), due to their high efficiency, long lifetime, absence of harmful substances, small footprint and high brightness [1, 2]. This is an evolution in both display backlighting and general lighting. The most common approach to achieve these (white) LEDs is by combining a blue pumping LED with one or more luminescent materials (or so-called phosphors) to yield the desired colour point. However, the specific LED-phosphor combination depends strongly on the type of application. For general lighting, one aims at a white emission colour (i.e. with specific colour temperature and with a colour point not deviating from the planckian locus) with a high colour rendering. Furthermore, the selected combination of a blue LED and phosphor(s) should have a high efficiency, which can be accomplished by a high quantum efficiency of the phosphors and an emission spectrum which is well-matched to the human eye sensitivity. For display backlighting, on the other hand, the spectral requirements are somewhat different [3]. In common display applications, saturated colours at the (sub)pixel level are needed. Therefore, the use of narrow band phosphors with saturated emission colours is preferred. Based on the general requirements for LED phosphors [4], mainly two dopant elements are suitable, namely Eu^{2+} and Ce^{3+}. Due to the spin orbit splitting of the ground state of the latter lanthanide ion, leading to an intrinsically broad emission spectrum, we focused our research onto divalent europium as a dopant.

2. MATERIALS AND METHODS

Thiogallate phosphors were prepared from appropriate precursor mixtures of Ga_2S_3, EuF_3, SrS and/or ZnS. These mixtures were heated at temperatures of typically 900-1000°C under H_2S atmosphere. More details can be found elsewhere [3]. X-ray diffraction was used to confirm phase purity. Luminescence characteristics were studied by steady-state fluorescence spectroscopy (emission and excitation) and lifetime measurements. Also, the influence of temperature on these characteristics was studied in the range from 75K to 475K. The microscopic homogeneity of the phosphor composition and the emission spectrum was verified by means of energy-dispersive x-ray analysis (EDX) and cathodoluminescence (CL) in a scanning electron microscope .

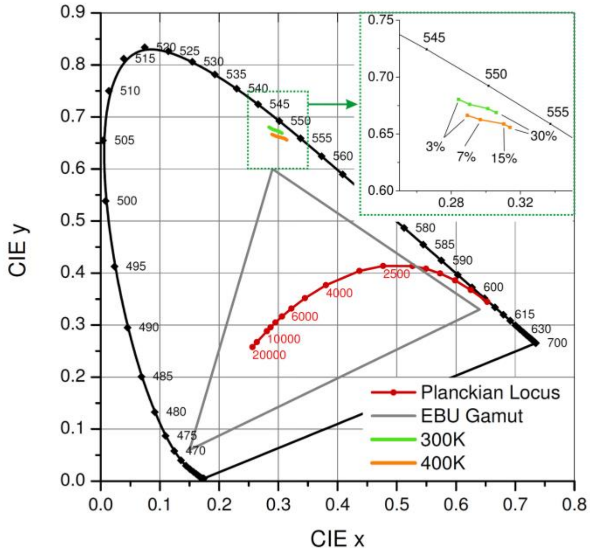

Figure 1. Colour coordinates of $Sr_{1-x}Eu_xGa_2S_4$ powders as function of temperature (300 K and 400 K) and dopant concentration. The black body locus and the EBU colour gamut are indicated as well. Adapted from [3].

3. RESULTS AND DISCUSSION

3.1 $SrGa_2S_4$:Eu

The luminescence properties of $SrGa_2S_4$ were evaluated over a wide dopant concentration range, with a 1 to 30% fraction of the Sr^{2+} ions substituted by Eu^{2+} .

The phosphors show a saturated green emission over the entire studied range, with a typical peak wavelength around 536 nm and a FWHM of 50 nm (Fig.1), which is in line with other reports [5, 6].

The optimum internal quantum efficiency is 71% for x = 0.04, although there is presumably still room for improvement by optimizing synthesis conditions. An important parameter is the thermal stability of the luminescence, in terms of both the emission spectrum and the emission efficiency.

For low dopant concentrations, the emission intensity at 400 K is still 90% of the intensity at room temperature. For higher dopant concentration, the thermal quenching gets worse. By studying the luminescence lifetime of these phosphors as function of the dopant concentration and the measurement temperature, we were able to show that two types of environment exist for the europium ions [3]. Due to the similar ionic radii for Sr^{2+} and Eu^{2+}, local dopant clustering can occur. At higher dopant concentrations, this provides more routes for energy transfer and non-radiative decay, which worsens the thermal quenching and lowers the quantum efficiency [3]. A further tuning of the emission properties of $SrGa_2S_4$:Eu is possible by (partial) substitution of Sr by Ca or Ba [7].

3.2. $ZnGa_2S_4$:Eu

There have been several reports in literature about narrow band emission in $ZnGa_2S_4$:Eu with the emission peaking at 540 nm [8]. However, we were able to show that europium-doped $ZnGa_2S_4$ shows hardly any luminescence. The observed green emission arises from an impurity phase, $EuGa_2S_4$, which is formed in the entire studied concentration range. This was proven by detailed analysis of x-ray diffraction patterns, luminescence lifetime measurements and an evaluation of the luminescence on a microscopic level, by means of cathodoluminescence spectroscopy in a scanning electron microscope (SEM-CL).

3.3. Stability issues

Most sulfide phosphors suffer from irreversible degradation upon exposure to moist air, due to hydrolysis. Strontium thiogallate is relatively stable, especially when compared to thioaluminates or most thiosilicates. We evaluated the stability of unprotected $SrGa_2S_4$:Eu phosphor powder during an accelerated ageing test in a controlled atmosphere (air, 80 °C, 80% relative humidity) and continuous monitoring of the photoluminescence (PL) intensity. After 100 h, the PL intensity had reduced to 81% of the initial value. By coating the phosphor with a thin layer of alumina, by means of atomic layer deposition (ALD) [9], the stability could strongly be improved (Fig. 2). Further assessment is still needed to evaluate the long term stability of this phosphor.

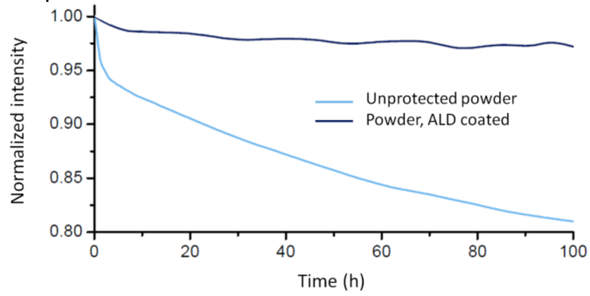

Figure 2. Stability of the photoluminescence of $SrGa_2S_4$:Eu powder with and without ALD coating during an accelerated ageing test (80°C, 80% relative humidity).

4. CONCLUSION

We have shown that europium-doped thiogallates are an interesting class of phosphors for use in LEDs, provided the stability issues – not uncommon for sulfide phosphors – can be overcome. Although $ZnGa_2S_4$:Eu had been reported in literature as a promising green phosphor, its efficiency is too low for applications, which is due to the formation of $EuGa_2S_4$. Coated $SrGa_2S_4$:Eu phosphors on the other hand are useful candidates to provide the green component in display backlighting.

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